The Use of Ugwuoba Clay as an Adsorbent for Zinc (II) Ions from Solution

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***Abstract*– The adsorption potential of Ugwuoba clay (Nigeria) for the removal of Zinc (II) ions from aqueous solution was studied. The aim of this experiment was the use of Ugwuoba clay as a cheap alternative adsorbent for Zinc (II) ions in order to assist small scale industries and developing Nations overcome the problems of high cost involved in treating effluents. Batch adsorption technique was used to investigate the effect of initial metal ion concentration, pH, contact time, Sorbent dose and temperature on the adsorption process. Chemical analysis of the clay showed SiO_2 and Al_2O_3 as the major constituents. FTIR analysis revealed some functional groups which could influence the adsorption process. The study on pH revealed the adsorption to be pH dependent as optimum pH was achieved at pH 6.0.Effect of contact time showed a fast initial uptake within 20 minute with equilibrium established before 60 minutes. Temperature experiment indicated an increase in adsorption with increase in temperature. An increase in uptake capacity and a decrease in percentage removal with increase in zinc (II) ion concentration was observed. Similarly, two opposite trend were noted in which there was an increase in percentage removal and a decrease in adsorption capacity with increasing sorbent dose. These result indicated that Ugwuoba clay can be used as a cheap and effective adsorbent for the removal of zinc (II) ions from aqueous solution.**

***Keywords*–** Adsorbent, Ugwuoba Clay, Zinc and Zn (II) Ions

I. INTRODUCTION

The growth of science and technology over the world has led to the establishment of various industries to help industrial, technological and agricultural development of many nations. As a result, pollution of our environment with waste generated from these industries have become a problem of major environmental concern. Heavy metal pollution is one of these problems because these metals tend to persist in nature, are non biodegradable, highly toxic and tend to accumulate causing different health problems to plants, animals and humans [1]. These heavy metals get to the environment through industrial activities such as battery manufacturing, cable coverings, radioactive shields, plumbing fixture, paints, pigment and paper production, textile industries, electroplating, print circuit boards, ceramics and glaze manufacturing, caulking and petroleum industries [2]. Zinc for instance is an essential micronutrient and is extensively used in galvanization and brass manufacturing. An excess of zinc can cause health problems such as stomach cramps, anemia, nausea and skin irritation. Very high concentration of zinc can damage the pancreas, upset protein metabolism resulting in arteriosclerosis. Also, high concentration of zinc in soils can lead to death of plants. Hence, the need to remove this metal from industrial wastewaters is necessary. Although traditional treatment methods such as reverse osmosis, chemical precipitation, ion exchange, chemical oxidation and reduction, evaporation, electrochemical treatment, filtration, solvent extraction and activated carbon adsorption have been used for the removal of Zinc and other heavy metals from effluents [3]. These techniques have the disadvantages of high cost, ineffective for the removal of metals at low concentrations, time consuming, require trained personnel, complicated and sometimes may generate toxic slurry which are difficult to eliminate. These reasons especially the high cost have limited the application of these techniques to developing Nations and small scale industries [4]. Therefore the need for a cheaper and more effective technology is required. Adsorption on low cost materials such as agricultural waste, biomass and clay have been performed by present day researchers and found to be effective, simple to handle and have a very low maintenance cost [5]. Some of the studies include the use of clay [6], biomass materials [7], [8], kaolinite [9] and geomaterials [10].

The main objective of the present study was to determine the feasibility of using easily available low cost material, in this case Ugwuoba clay as an adsorbent for the removal of zinc(II) ions from aqueous solution. Ugwuoba clay is found in large deposits in Ugwuoba in Oji River local government area of Enugu state, Nigeria and can easily be obtained with little or no cost. The effect of solution pH, initial metal ion concentration, contact time, sorbent dose and temperature were determined in this study.

II. MATERIALS AND METHODS

A. Sample Preparation and Characterization

Ugwuoba clay was collected from Oji River local government area of Enugu state, Nigeria. The clay was dispersed in distilled water in a plastic container. The dispersed clay was stirred and then sieved in order to remove plant materials and unwanted suspended particles. The filtrate was allowed to settle for 24hrs to allow sedimentation after which excess water was decanted from the top of the container. The clay obtained was sundried for several days, then oven dried at 100^0C for 2hrs, pulverized and sieved using a 100µm mesh sieve. The sample was then ready for use as an adsorbent.

The chemical characterization of the clay was determined using classical method. Fourier Transform Infrared (FTIR) spectra of the clay was determined using the FTIR Spectrophotometer (Shimadzu FTIR 8400S) in the wave number range of 400-4000cm^{-1}.

B. Preparation of Zinc(II) Ion Solution

All the chemicals used in this study were analytical grade. A stock solution of zinc(II) ion was prepared by dissolving accurate quantity of Zinc sulphate ($ZnSO_4.7H_2O$) in de-ionized water. Other concentrations ranging from 20-100mg/L were prepared from this stock solution by dilution. The pH of the solution was adjusted to the desired values with drop wise addition of 0.1M HNO_3 or 0.1M NaOH by the use of a pH meter. Fresh dilution was used for each experiment.

C. Adsorption Procedure

The adsorption study was carried to determine the effect of solution pH, sorbent dose, contact time , initial Zn ion concentration and temperature using batch technique. This was performed at different pH values of (1-8), initial zinc(II) ion concentrations of 20, 40, 60, 80 and 100mg/L, contact time of 10-120 minutes, temperature of 27, 30, 35, 40 and 45^0C and sorbent dose of 0.5-2.5g. The experiment was performed by adding 2g of Ugwuoba clay to 20mls of a given Zn(II) ion solution . It was placed in a thermostated water bath (Hakke Wia Model) in order to regulate the temperature and left for a contact time of 2 hours to ensure equilibrium was achieved after which the mixture was filtered. The filtrate was analyzed for residual Zn(II) concentration by the use of the Atomic Absorption Spectrophotometer (AAS) (Buck Scientific model 210 VGP). Each experiment was performed in duplicate and the mean value was determined. The amount of Zn(II) ion adsorbed by the clay in milligram per gram was determined by using the mass balance equation given in (1).

$$qe = \frac{V(C_o - C_e)}{m} \qquad (1)$$

where qe is the amount of zinc ion absorbed per unit weight of the adsorbent in mg/g. C_o is initial concentration of zinc ion in mg/L, C_e is the equilibrium metal ion concentration in mg/L, V is the amount of adsorbate in Liters and m is the mass of the adsorbent in grams. The percentage removal of Zinc(II) ions removed by the clay was calculated from (2).

$$Removal\ (\%) = \frac{C_o - C_e}{C_o} \times 100 \qquad (2)$$

III. RESULT AND DISCUSSION

A. Chemical Composition of Ugwuoba Clay

The chemical characterization of Ugwuoba clay as determined by classical method is shown in Table I. The result indicated the presence of Silica, Alumina, Calcium, Sodium and magnesium oxide as major constituents, while other elements such as Iron(III) oxide, Potassium oxide and manganese oxide are present in smaller amount . Therefore the adsorbate species in solution are expected to be removed mainly by SiO_2 and Al_2O_3.

B. FTIR Analysis

The FTIR spectra was used to determine the nature of functional groups which could possibly influence the adsorption ability of the clay. The FTIR spectra of Ugwuoba clay is shown in Fig 1. It is observed that the spectra did not display a large number of adsorption peaks. However, some peaks were observed which confirms the presence of certain functional groups on the clay surface. The band at 2250cm^{-1} showed the presence of C≡N. The peak at 1632cm^{-1} is indicative of a C=C of alkenes. Also, the peak observed at 1105cm^{-1} corresponds to C-O stretching vibrations. The band at 1028cm^{-1} represents the Si-O stretching in the Si-O-Si group of the tetrahedral sheet of the clay [11]. The bands indicated at 696cm^{-1} and 546cm^{-1} represents the C-Cl and C-Br stretching vibrations. This results indicated that the clay material have some functional groups and surface structures with electron density available for binding to the positive zinc(II) ions in solution.

C. Effect of pH

The initial pH of a solution is the most significant factor in the sorption of heavy metals as it has a major effect on the protonation and deprotonation of the active sites and functional groups of an adsorbent which greatly influences sorption. Fig. 2 shows the effect of pH on the sorption of zinc(II) ions on ugwuoba clay. The result showed an increase in adsorption capacity with increase in pH and maximum adsorption was obtained at pH 6.0 after which it decreases slightly up to 8.0. The pH, 6.0 was selected as the optimum pH for the removal of Zinc(II) ions by ugwuoba clay and subsequent experiments were conducted at this pH. The pH determines the charge on the adsorbent and this determines the bind ability of metal ions to the surface. The mechanism of sorption on the surface of an adsorbent reflects the physiochemical interaction of the metal ions in solutions and binding sites on the adsorbent [12]. The active sites on the surface of the clay are protonated at lower pH values which restricts the approach of positively charged metal ions to the surface of the clay, hence results in decrease in the adsorption of Zinc(II) ions. This is because the metal ions compete with the protons for the active sites on the adsorbent. As the pH increases, the active sites on the clay becomes deprotonated and free for Zinc(II) ions to bind. Consequently, the competition between the protons and metal ions for the active sites is reduced, resulting in an increase in uptake capacity with increase in pH [13]. At higher pH values greater than 7 in the alkaline region, several hydroxyl, 1ow soluble species can be precipitated such as $Zn(OH)_2$ or $Zn(OH)_3$, this account for the reason why the alkaline region is usually avoided in most adsorption studies to avoid metal precipitation. Adsorption process is reversible in the presence of mineral acid due to its ability to regulate the net charge on the surface of the adsorbent, this explains why desorption of already adsorbed metal ions is possible [14]. Similar result on the increase in adsorption with pH has been reported [15].

D. The Effect of Sorbent Dose

The study investigated the effect of sorbent dose by varying the amount of clay from 0.5 to 2.5g which was contacted with a fixed concentration of zinc(II) ion at 20mg/L. The result on the effect of adsorbent dose on the sorption of zinc(II) ions is shown in Fig 3 and Fig 4. Fig 3 shows the effect of sorbent dose as a function of the percentage removal while Fig 4 relates this factor to the adsorption capacity (mg/g) of the clay. As seen in Fig 3, it was observed that the percentage of zinc(II) ion removed increased with increase in sorbent dose. This may be attributed to increase in surface negative charge and a decrease in the electrostatic potential near the solid surface which favors adsorbent-adsorbate interactions [16]. It is also due to the availability of more active sites on the surface of the sorbent. However, Fig. 4 showed an opposite trend, a decrease in adsorption capacity with increase in sorbent dose was observed. This may be as a result of a decrease in the total sorption surface area available for zinc(II) ions to bind due to aggregation or overlapping of active sites [17]. This reason along with the availability of solute and electrostatic interactions have been recommended to explain the trend of decrease in adsorption capacity [18]. Thus increasing the adsorbent dose led to a decrease in the amount of zinc(II) adsorbed per unit mass of the adsorbent leading to the reduction in *qe* values. Furthermore, the increase in the amount adsorbed when the amount of clay used was increased from 2.0-2.5g was negligible. This may be due to the establishment of equilibrium between zinc(II) ions in solution and on ugwuoba clay. Similar result has been reported [19].

E. Influence of Temperature

The effect of temperature on the adsorption of zinc(II) ions on ugwuoba clay was investigated. The result is shown in Fig. 5. This result indicated that as the temperature of the solution was increased from 27-45^{0}C, there was also a corresponding increase in the amount of zinc(II) ions adsorbed by the clay. This increase in adsorption capacity with increase in temperature indicated that the adsorption process is endothermic in nature, it also suggest a chemisorptions process i.e adsorption accompanied by a chemical reaction. It is restricted to just on layer of molecules on the surface but may be followed by an additional layer of physically adsorbed metal ions [20]. Similar result has been reported [16], [21]. A good literature search has revealed different types of results on the effect of temperature on the adsorption of heavy metals. A decrease in adsorption potential with increase in temperature has been observed [22]. Temperature-independent effect on adsorption has also been recorded [23].

F. Effect of Initial Adsorbate Concentration

The result on the effect of initial concentration of zinc(II) ion on its adsorption by ugwuoba clay is shown in Fig 6 and 7. Fig. 6 expresses the plot of adsorption uptake capacity qe(mg/g) as a function of the initial concentration of Zinc while Fig. 7 represents its effect on the percentage removal . it is observed from Fig. 6 that an increase in adsorption capacity with increase in initial concentration was obtained. This is due to the fact that more metal ions were available for binding to the active sites of the clay. The increase in the concentration of metal ions led to an increase in collision between the ions and adsorbent hence increased the driving force to overcome resistance to mass transfer and thus an increase in uptake capacity [24]. However, a decrease in the percentage removal with increase in the concentration of zinc(II) ion was observed in Fig. 7. This can be accounted for that all adsorbents have a limited or fixed number of active sites and at a certain metal ion concentration the active sites becomes used up and saturated [25]. This implies that further increase in the concentration of zinc(II) ion will only led to a decrease in the percentage removal as the actives are already occupied, hence more metal ions will be remaining in solution after adsorption. Using calcareous soil, similar result has been observed [26].

G. Effect of Time on Adsorption

The influence of time is also an important factor to be considered on the adsorption of metal ions by an adsorbent. It has been reported that the contact time plays an important role in adsorption process [27]. The sorption of zinc(II) ions on ugwuoba clay as a function of time is shown in Fig 8. A sharp increase in the adsorption was noticed within the first twenty minutes after which it increased slightly up to 50 minutes. After 50 minutes there was no significant increase in the uptake capacity with further increase in time which suggests that equilibrium have been obtained. In the present study, 2hrs was used as the contact time for all the experiments, hence we ensured that equilibrium was attained. The fast rate of adsorption observed at the initial stage may be explained by an availability of abundant active sites on the adsorbent surface which gradually became occupied with time. As these sites are progressively filled the more difficult the sorption becomes as the process tends to become unfavorable [28]. The changes in the fast and then gradual uptake of metal ion may be due to two types of adsorption mechanisms, the first involves a fast ion exchange mechanism followed by a second which is chemisorptions[29]. Other researchers have obtained similar results [19], [26], [30].

IV. CONCLUSION

The result of this study indicated that Ugwuoba clay can be used as a cheap and effective adsorbent for the removal of Zinc (II) ions from aqueous solution. FTIR analysis of the clay revealed the presence of some functional groups which could influence the adsorption process. The experimental parameters studied such as pH, adsorbent dose, temperature, initial Zinc (II) ion concentration and time all proved to be important parameters in the description of the sorption process.

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TABLE I: CHEMICAL CHARACTERIZATION OF UGWUOBA CLAY

Composition	SiO_2	Al_2O_3	CaO	MgO	Na_2O_3	Fe_2O_3	K_2O	MnO	Loss on Ignition
% by Weight	47.32	25.91	4.39	3.14	2.86	1.14	1.07	0.43	13.56

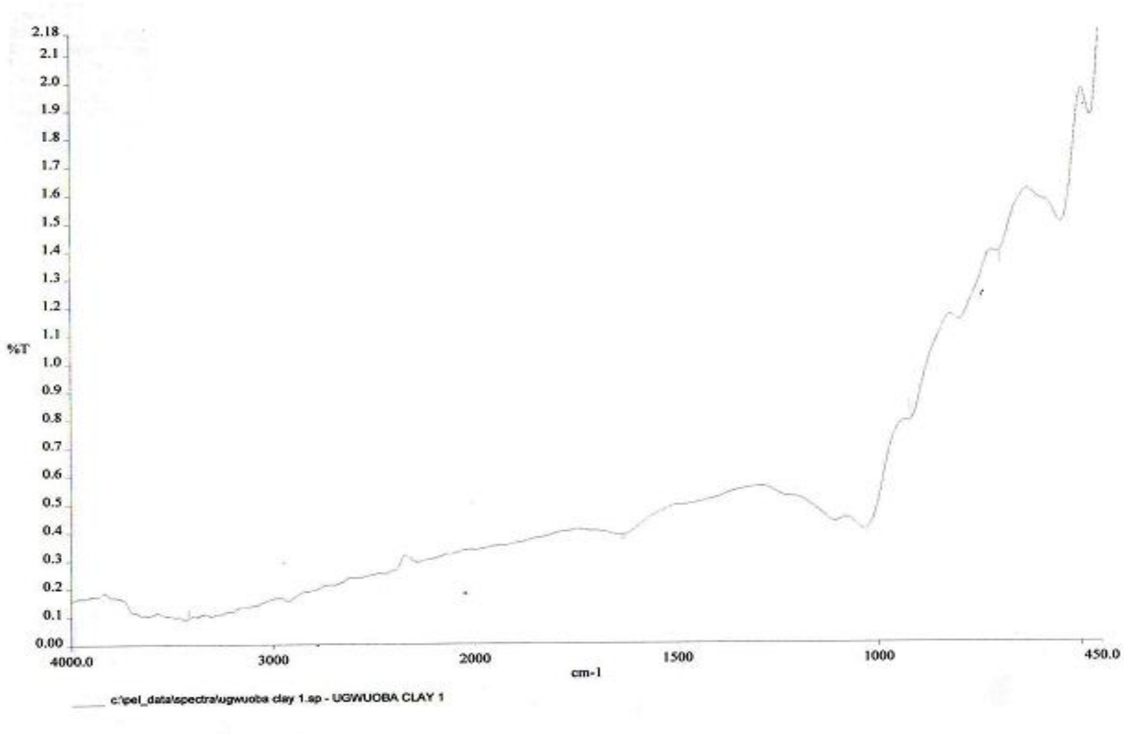

Fig. 1: FTIR Spectrum of Ugwuoba Clay

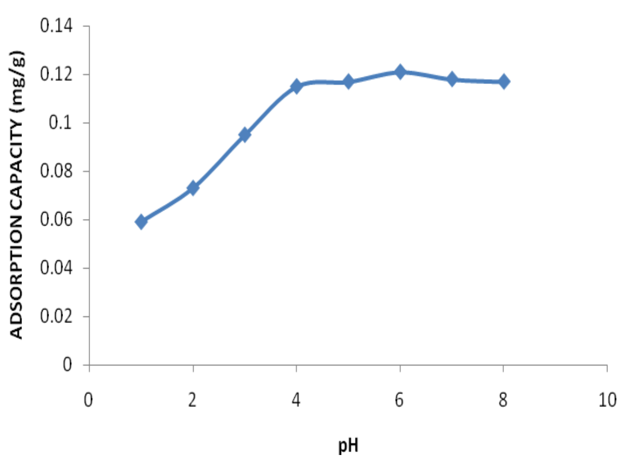

Fig. 2: Inluence of pH on the adsorption of Zinc(II) ions on Ugwuoba clay (Initial conc, 20mg/L, Contact time 2hrs, Sorbent dose 2g, Temperature 300K)

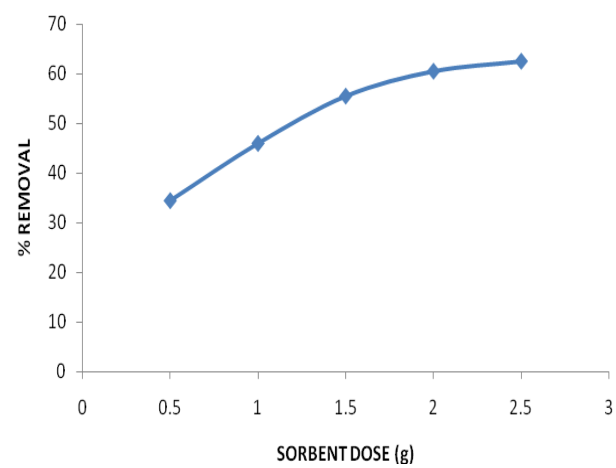

Fig 3: Influence of Sorbent dose on the adsorption of Zinc(II) ions on Ugwuoba clay expressed in terms of perentage removal (Initial conc 20mg/L, Contact time 2hrs, pH 6.0, Temperature 300K)

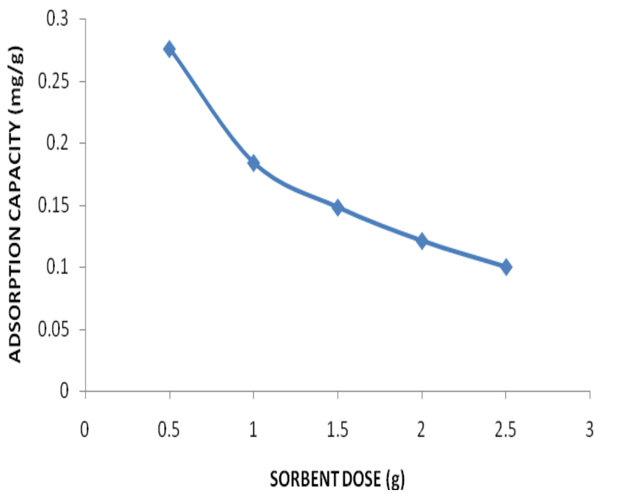

Fig. 4: Influence of Sorbent dose on the adsorption of Zinc(II) ions on Ugwuoba clay (Initial conc 20mg/L, Contact time 2hrs, pH 6.0, Temperature 300K)

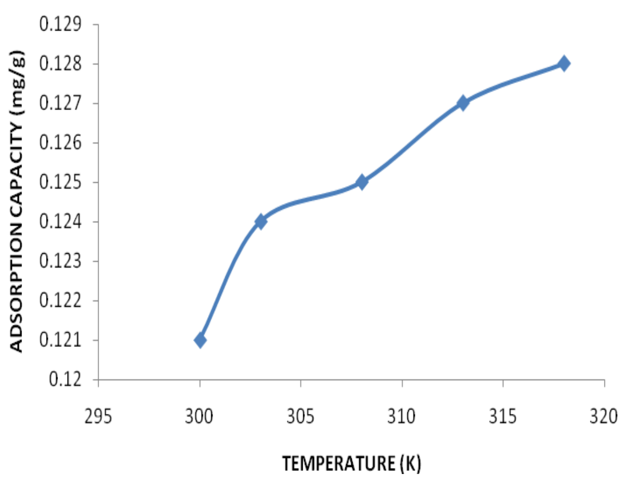

Fig. 5: Influence of Temperature on the adsorption of Zinc(II) ions on Ugwuoba clay (Initial conc 20mg/L, Contact time 2hrs, pH 6.0, Sorbent dose 2g)

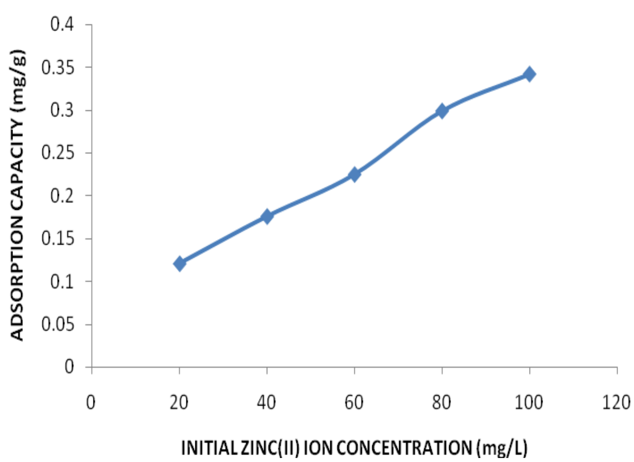

Fig. 6: Influence of Initial Zinc(II) ion concentration on the adsorption of Zinc(II) ions on Ugwuoba clay (Temperature 300K, Contact time 2hrs, pH 6.0, Sorbent dose)

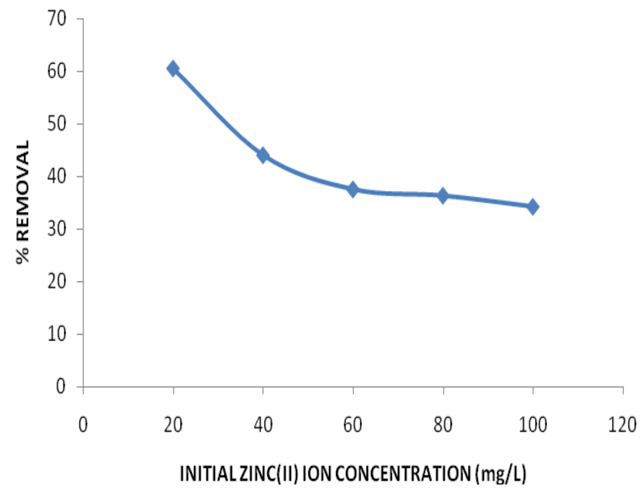

Fig.7: Influence of Initial Zinc(II) ion concentration on the adsorption of Zinc(II) ions on Ugwuoba clay, expressed as percentage removed (Temperature Fig 300K, Contact time 2hrs, pH 6.0, Sorbent dose 2g)

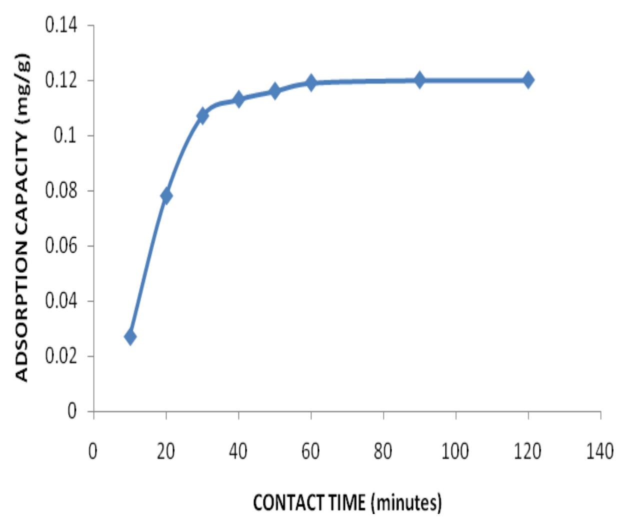

Fig.8: Influence of Contact time on the adsorption of Zinc(II) ions on Ugwuoba clay (Initial conc 20mg/L, Temperature 300K, pH 6.0,Sorbentdose2g)